

I. THE CLAISEN REARRANGEMENT
AND STERIC HINDRANCE

II. THE ADDITION OF GRIGNARD
REAGENTS TO BENZOFULVENES

BY

FRANKLIN EDWARD MUMFORD

B.A., University of South Dakota, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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PART ONE

THE CLAISEN REARRANGEMENT AND STERIC HINDRANCE

INTRODUCTION

The Claisen rearrangement of suitably constituted aromatic ethers offers an attractive route to highly hindered molecules since the allyl group migrates by an intramolecular reaction (1). In the triarylcarbinol series, for example, the rearrangement of the allyl group in 2,4-dimethyl-5-allyloxyphenylmesitylphenylcarbinol would produce a carbinol with 2,6,2',6' alkyl substituents. This extreme degree of hindrance cannot be obtained through addition of aryl organometallic compounds to the properly substituted benzophenones (2, 3).

In the present work, several triarylcarbinols were synthesized in which one of the aryl groups was the 2, 4-dimethyl-5-allyloxyphenyl radical, and attempts were made to effect a Claisen rearrangement in these molecules.

DISCUSSION OF RESULTS

2,4-Dimethyl-5-allyloxyphenylmesitylphenylcarbinol and 2,4-dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol were prepared through the condensation of 2,4-dimethyl-5-allyloxybenzophenone with mesityllithium and *o*-tolyllithium, respectively. It was found that the mesityl substituted carbinol did not rearrange on being heated at 200° for one hour. More drastic treatment converted it to resinous materials. Possibly the rearrangement failed because of the steric requirements of the mesityl group, although models of 2,4-dimethyl-5-hydroxy-6-allylphenylmesitylphenylcarbinol indicated that it is perfectly capable of existence. Moreover, the rearrangement also failed in 2,4-dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol, a molecule in which space exigency is not great.

2,4-Dimethyl-5-allyloxybenzophenone was prepared from

the corresponding methyl ether which had been made by Meisenheimer, Hanssen and Wächterowitz (4) by benzylation of 2,4-dimethylanisole in the presence of aluminum chloride. Treatment of the methyl ether with hydriodic acid converted it to the corresponding hydroxy ketone, which was allylated with allyl bromide in the presence of potassium carbonate. It is of interest that this allyl ether rearranges readily to 2,4-dimethyl-5-hydroxy-6-allylbenzophenone, for it confirms the surprising finding of Meisenheimer, et. al., that the benzoyl group introduced into 2,4-dimethylanisole by the method of Friedel and Crafts is situated in a position *meta* to the methoxyl group. The rearrangement is unusual in that the aromatic nucleus involved bears a *meta*-directing group in a position *meta* to the allyloxyl group.

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PART TWO

THE ADDITION OF GRIGNARD REAGENTS TO BENZOFULVENES

INTRODUCTION

The first confirmed addition of a Grignard reagent to a carbon-carbon double bond not conjugated with a carbonyl group was reported by Fuson and Porter in 1948 (1). In this case the active Grignard reagents, *t*-butylmagnesium chloride

and benzylmagnesium chloride, were condensed with the highly conjugated olefin, dibiphenyleneethylene. More recently these same Grignard reagents have been added to two vinyls of dibiphenyleneethylene, namely, 1,4-dibiphenylene-1,3-butadiene and 1,6-dibiphenylene-1,3,5-hexatriene (2). The unique capacity of these molecules to add the more active Grignard reagents is undoubtedly due to the cyclopentadiene nucleus which, because of its great affinity for an electron pair (3), provides for a high degree of polarization of the semicyclic double bond. Thus 5-methylenecyclopentadiene, or fulvene as it is more generally designated, should be capable of adding Grignard reagents.

In the present work a study of the reactivity of several benzofulvenes towards various Grignard reagents was undertaken.

DISCUSSION OF RESULTS

t-Butylmagnesium chloride added to 2,3-diphenylbenzofulvene and dibenzofulvene to give 1-neopentyl-2,3-diphenylbenzofulvene and 9-neopentylfluorene, respectively. The structure of the former was proven by an independent synthesis involving well known procedures. Although no adduct was isolated when 2,3-diphenylbenzofulvene was treated with benzylmagnesium chloride, dibenzofulvene condensed with benzylmagnesium chloride to give two products. The structure of these compounds has not been determined.

A surprising result was observed when 2,3-diphenylbenzofulvene was treated with a Grignard reagent in which excess magnesium metal was present. A high-melting, white, crystalline product was isolated which apparently did not contain the alkyl group from the alkylmagnesium halide, since the same material was obtained regardless of the Grignard reagent used. Under these same conditions benzophenone is known to undergo a bimolecular reduction to a pinacol (4). In view of the similarity of the $\text{CH}_2 = \text{C} =$ bond in a fulvene to the $= \text{C} = \text{O}$ bond in benzophenone, the hydrocarbon pre-

pared in these reactions may be the bimolecular reduction product of 2,3-diphenylbenzofulvene. Indeed, such a reaction has been observed with acenaphthylene (5).

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VITA

The author was born in Howard, South Dakota, on July 25, 1926. He attended grammar school there, and was graduated from Howard High School in 1944. He entered the University of South Dakota in June of the same year, and received the Bachelor of Arts degree in June, 1947. He entered the Graduate School at the University of Illinois in September, 1947. From that time to June, 1949 he was a half-time teaching assistant. From September, 1949, to June, 1951, he held a University fellowship. During the summer of 1950 he was employed at the DuPont Experimental Station in Wilmington, Delaware.



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